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Simulating the Ultrafast Excited State Dynamics of Cyclopentadiene and 1,2,3,4-tetramethylcyclopentadiene

Thomas S. Kuhlman†, Will J. Glover ‡, Toshifumi Mori ‡, Klaus B. Møller†, and Todd J. Martínez‡

† *Department of Chemistry, Technical University of Denmark, DTU Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark*

‡ *Department of Chemistry and PULSE Institute, Stanford University, Stanford, CA 94305, USA, and SLAC National Accelerator Laboratory, Menlo Park, CA 94309, USA*

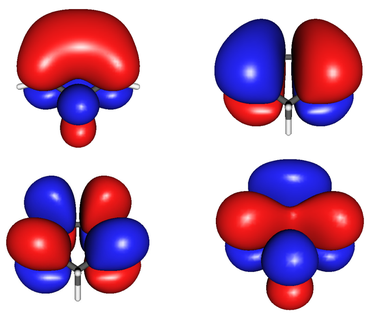
Introduction

Motivation

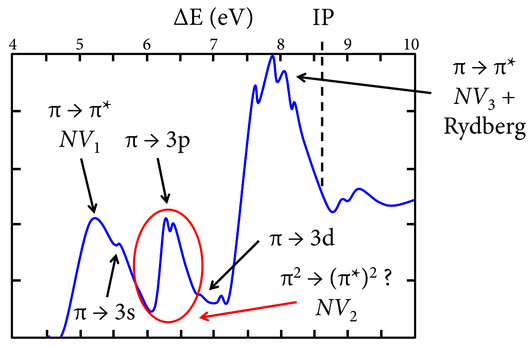
- Polyenes like cyclopentadiene are ubiquitous as chromophores in diverse areas ranging from light harvesting and the vision process to devices such as light emitting diodes
- Polyenes possess low-lying optically dark states with large doubly excited character, which give rise to the observation of ultrafast excited state dynamics in the form of non-diabatic dynamics

Focus

- Elucidate on structure-dynamics relationships focused on the influence of specific nuclear motion and substituents effects on dynamics at conical intersections
- Correlate dynamics simulations using Ab Initio Multiple Spawning[2] with experimental data from time-resolved mass spectrometry and photoelectron spectroscopy



The two π- and two π*-molecular orbitals of cyclopentadiene from HOMO-1 to LUMO+1



Electronic spectrum of cyclopentadiene with indication of different transitions[1]

Methods

Ab Initio Mulitple Spawning

- Nuclear time-dependent Schrödinger equation solved in a basis of gaussians (TBF)
- Electronic structure is calculated *on-the-fly*
- Parameters of basis functions χ^J_j propagated according to Hamiltons equations
- Coefficients $C^J_j(t)$ of wave function $X_J(\mathbf{R},t)$ propagated quantum mechanically
- New basis functions optimally *spawned* when coupling between surfaces is large

- Basis function :

$$\chi^J_{j\eta}(R_\eta;\overline{R}^J_{j\eta}(t),\overline{P}^J_{j\eta}(t),\alpha^J_{j\eta}) = \left(\frac{2\alpha^J_{j\eta}}{\pi}\right)^{1/4} \exp\left[-\alpha^J_{j\eta}(R_\eta-\overline{R}^J_{j\eta}(t))^2 + i\overline{P}^J_{j\eta}(t)(R_\eta-\overline{R}^J_{j\eta}(t))\right]$$

$$\chi^J_j(\mathbf{R};\overline{\mathbf{R}}^J_j(t),\overline{\mathbf{P}}^J_j(t),\bar{\gamma}^J_j(t),\alpha^J_j) = e^{i\bar{\gamma}^J_j(t)} \prod_\eta^{3N_{\text{atom}}} \chi^J_{j\eta}(R_\eta;\overline{R}^J_{j\eta}(t),\overline{P}^J_{j\eta}(t),\alpha^J_{j\eta})$$

- Wave function :

$$X_J(\mathbf{R},t) = \sum_j^{N_J(t)} C^J_j(t)\chi^J_j\left(\mathbf{R};\overline{\mathbf{R}}^J_j(t),\overline{\mathbf{P}}^J_j(t),\bar{\gamma}^J_j(t),\alpha^J_j\right)$$

- Working eqs.

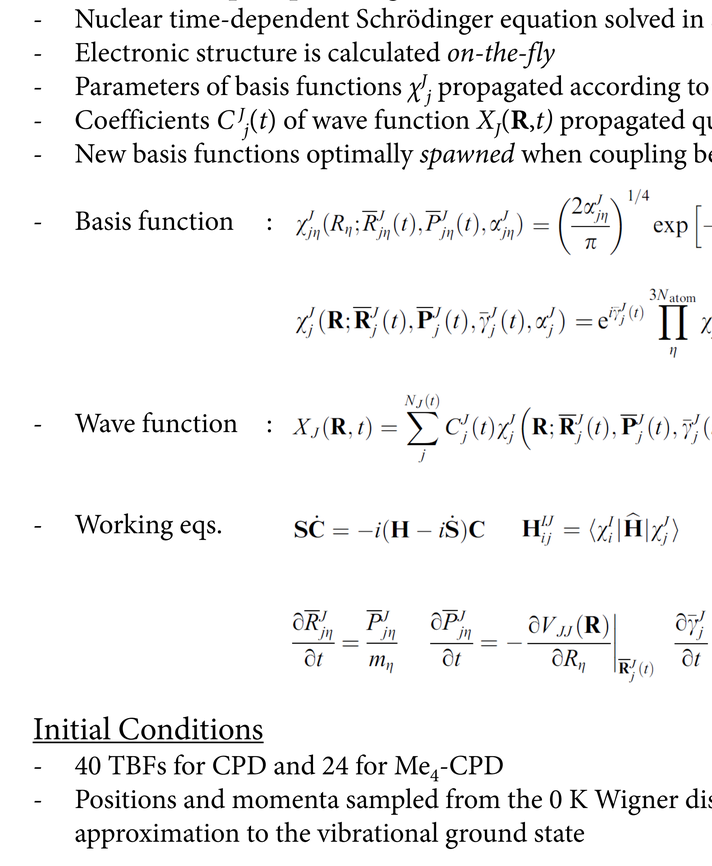
$$\mathbf{S}\dot{\mathbf{C}} = -i(\mathbf{H}-i\dot{\mathbf{S}})\mathbf{C} \qquad \mathbf{H}^{IJ}_{ij} = \langle\chi^I_i|\hat{\mathbf{H}}|\chi^J_j\rangle \qquad \mathbf{S}^{IJ}_{ij} = \langle\chi^I_i|\chi^J_j\rangle\delta_{IJ} \qquad \dot{\mathbf{S}}^{IJ}_{ij} = \left\langle\chi^I_i\middle|\frac{\partial}{\partial t}\chi^J_j\right\rangle\delta_{IJ}$$

$$\frac{\partial\overline{R}^J_{j\eta}}{\partial t} = \frac{\overline{P}^J_{j\eta}}{m_\eta} \qquad \frac{\partial\overline{P}^J_{j\eta}}{\partial t} = -\left.\frac{\partial V_{JJ}(\mathbf{R})}{\partial R_\eta}\right|_{\overline{\mathbf{R}}^J_j(t)} \qquad \frac{\partial\bar{\gamma}^J_j}{\partial t} = -V_{JJ}(\overline{\mathbf{R}}(t)) + \sum_\eta^{3N}\frac{\left(\overline{P}^J_{j\eta}(t)\right)^2}{2m_\eta}$$

Initial Conditions

- 40 TBFs for CPD and 24 for Me_4-CPD
- Positions and momenta sampled from the 0 K Wigner distribution of the harmonic approximation to the vibrational ground state

Electronic Structure

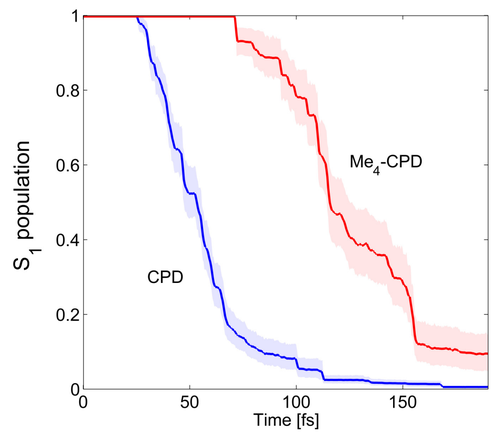


- MS-3-MR-CASPT2/6-31G** with a (4,4) active space
- Analytic non-adiabatic couplings[3]
- Four Minimum Energy Conical Intersections (MECIs) located – three between S_1 and S_0 and one between S_2 and S_1
- No minimum (zero gradient) located for neither S_1 nor S_2 as the minimum energy configuration located for both states is an MECI

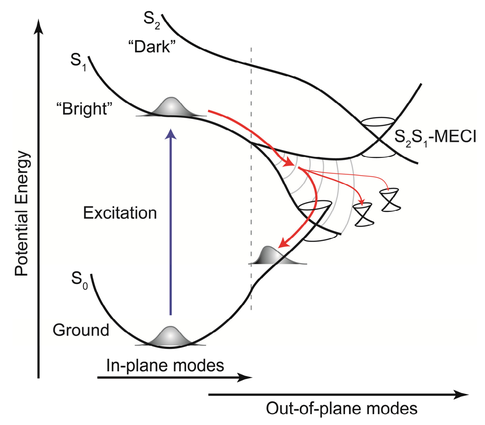
References

1. R. P. Frueholz et al., J. Chem. Phys., **1979**, *70*, 2003-2013
2. M. Ben-Nun, T. J. Martinez, Adv. Chem. Phys., **2002**, *121*, 439-512
3. T. Mori et al., J. Phys. Chem. A, **2012**, *116*, 2808-2818

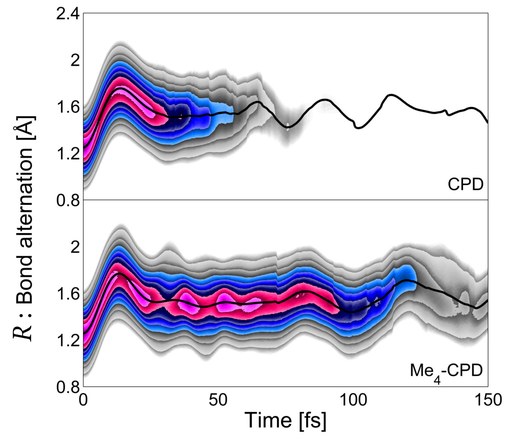
Dynamics following Excitation to S_1



Decay of S_1 population in CPD and Me_4-CPD.

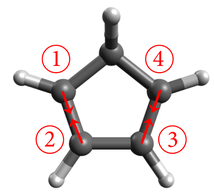


Scheme of the dynamics following excitation to S_1 as observed in the calculations.

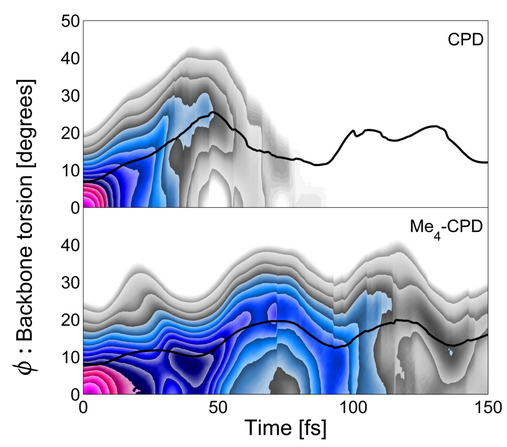


Bond Alternation

- Initial nuclear motion is primarily in-plane with no significant difference between the two molecules.

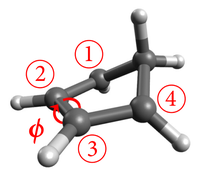


$$R = R_{12} + R_{34} - R_{23}$$

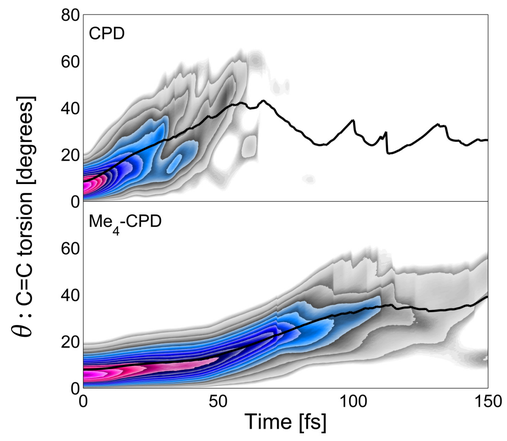


Backbone Distortion

- Out-of-plane distortion of the backbone is observed but the expectation value is similar in the two molecules for times > 50 fs.

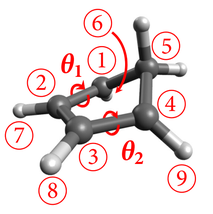


$$\phi = \angle C_1C_2C_3C_4$$



Double Bond Twist

- A siginificant slower torsion in the double bonds is observed for Me_4-CPD compared to CPD.



$$\theta = \max[\theta_1, \theta_2]$$

$$\theta_1 = \cos^{-1}[(\mathbf{R}_{12}\times\mathbf{R}_{56})\cdot(\mathbf{R}_{12}\times\mathbf{R}_{37})]$$

$$\theta_2 = \cos^{-1}[(\mathbf{R}_{34}\times\mathbf{R}_{28})\cdot(\mathbf{R}_{34}\times\mathbf{R}_{59})]$$

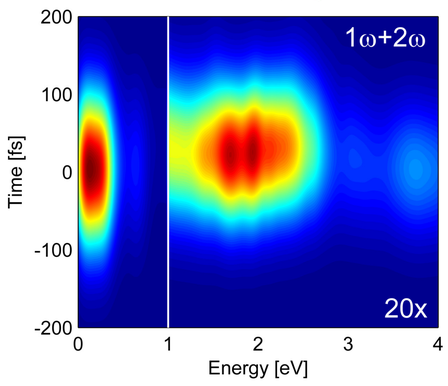
Time scale ~ 20 fs
~ 50 fs
~ 100 fs

Time-Resolved Photoelectron Spectra

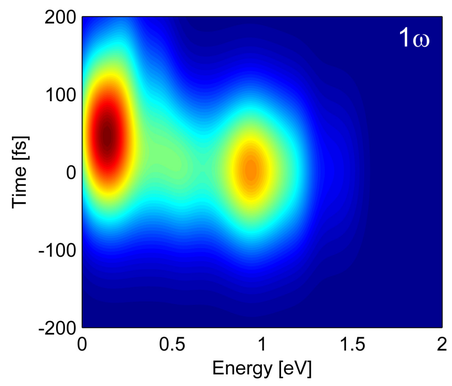
- The dipole matrix element connecting the initial neutral state *I* and final cationic state *F* is evaluated in the single-active electron approximation using the strong orthogonality condition

$$\langle\Psi^N_I(\mathbf{r}_1,\ldots,\mathbf{r}_N)|\hat{\mu}(\mathbf{r}_1,\ldots,\mathbf{r}_N)|\Psi^{N-1}_F(\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi^{el}_{kf}(\mathbf{r}_1)\rangle = \langle\phi^D_{IF}(\mathbf{r}_1)|\hat{\mu}(\mathbf{r}_1)|\Psi^{el}_{kf}(\mathbf{r}_1)\rangle_{\mathbf{r}_1}$$

$$\sigma_{\text{stick}}(E_k,\Delta t) \propto \sum_{I,F}\sum_f \left|\mathcal{E}_\omega(\Delta t)\cdot\langle\phi^D_{IF}(\mathbf{r}_1)|\hat{\mu}(\mathbf{r}_1)|\Psi^{el}_{kf}(\mathbf{r}_1)\rangle_{\mathbf{r}_1}\right|^2 \delta([\hbar\omega-\Delta E]-E_k)$$



Combined 1- and 2-photon spectrum for CPD. The band above 1 eV results from 2-photon ionization. Both observed bands are due to ionization out of the S_1 state.



1-photon spectrum for Me_4-CPD. Both observed bands are due to ionization out of the S_1 state.